

9572 WO

(12) UK Patent Application (19) GB (11) 2 028 329 A

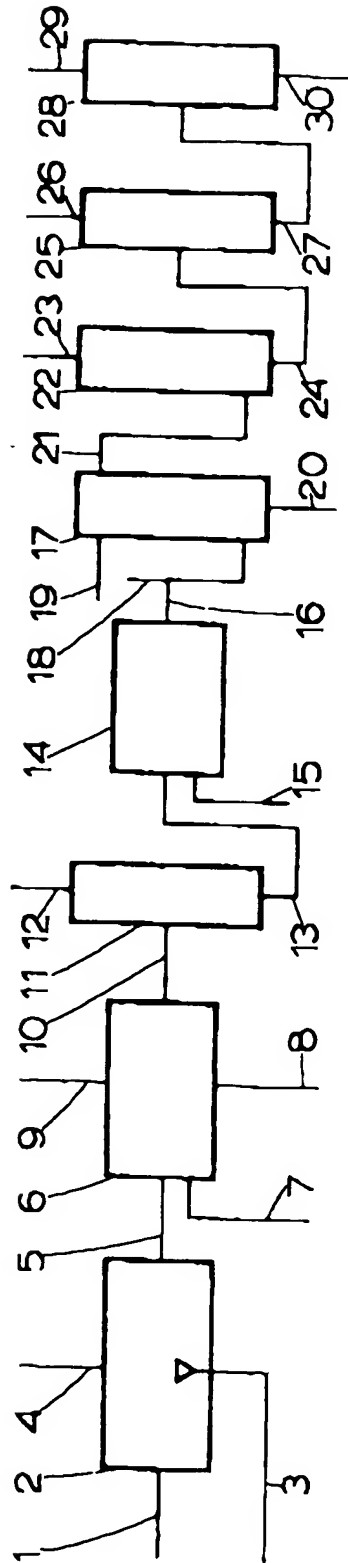
- (21) Application No 7928080
(22) Date of filing 13 Aug 1979
(28) Claims filed 13 Aug 1979
(30) Priority data
(31) 7808416
(32) 12 Aug 1978
(33) Netherlands (NL)
(43) Application published
5 Mar 1980
(51) INT CL³
C07C 45/78 45/33 48/285
(52) Domestic classification
C2C 1175 1177 221 225
227 22Y 297 30Y 351 353
386 409 40Y 413 416 43X
625 GX UE
(58) Documents cited
GB 1420511
GB 1104180
GB 1060484
GB 1018557
(58) Field of search
C2C
(71) Applicants
Stamloarbon B.V., P.O.
Box 10, Geleen, the
Netherlands
(72) Inventor
Otto Gerrit Plantema
(74) Agents
Hyda, Heide & O'Donnell

(54) Purification of cycloalkanones
obtained by oxidation of
cycloalkanes

(57) The purification of a C₆-C₁₂ cycloalkanone e.g. cycloalkane, obtained by oxidation of the corresponding cycloalkane, is effected by subjecting the cycloalkanone to an aldol condensation whereby at least 80% of the aldehydes present are converted but not more than 20% of cycloalkyl esters derived from carboxylic acids containing at least 4 carbon atoms per molecule, is allowed to saponify. In effecting the aldol condensation an alkaline catalyst may be used, e.g. sodium hydroxide or sodium carbonate, or an acid catalyst may be used e.g. sulphuric acid or an acid ion exchanger. After the aldol condensation has been effected the cycloalkanone may be separated by distillation.

GB 2 028 329 A

2028323



SPECIFICATION

Process for the purification of cycloalkanone mixtures obtained in the oxidation of cycloalkanes

5

The invention relates to a process for the purification of mixtures that contain a cycloalkanone containing 5-12 carbon atoms in the ring and which have been obtained by the oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen.

The preparation of cycloalkanone mixtures by oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen is well known (see, e.g., the general surveys in the Stanford Research Institute Reports 3 (1965), 34 (1971), 7 (1965), 307-319, and 74 (1968), 87-103). In most cases use is made of a degree of conversion of 1-12% calculated to the cycloalkane feed stock, so that the resulting reaction mixture contains a large proportion of unconverted cycloalkane. The mixture furthermore contains, in addition to the cycloalkanone a considerable amount of the corresponding cycloalkanol in most instances, and a minor proportion of secondary products, including aldehydes, organic acids and cycloalkyl esters. It is common practice to process the reaction mixture by distillation, when the cycloalkane and the by-products that are more volatile than the cycloalkane, and including a large part of the aldehydes, are distilled off first, followed by the cycloalkanone and finally the cycloalkanol. The residue consists of high-boiling cycloalkyl esters and other products.

According to a known process procedure the yield of cycloalkanol is improved by saponifying the cycloalkyl esters present in the reaction mixture after distillation of the cycloalkane by treatment with an aqueous solution of sodium hydroxide or sodium carbonate. This process has the disadvantage, that the stringent conditions required for the saponification of the high-boiling cycloalkyl esters, which are difficult to saponify, cause the cycloalkanol to be converted by self-condensation into the corresponding 2-cycloalkylidene cycloalkanone, thus becomes lost (Netherlands published Patent Application 6600638). The remedy for this problem is to wash the reaction mixture with dilute aqueous solutions of alkali hydroxides or alkali carbonates under such mild conditions that only the organic acids dissolved in the organic phase are neutralized and no saponification of cycloalkyl esters is effected. The product thus obtained is distilled and then saponified with an aqueous alkali solution. By this means of loss of cycloalkanone by self-condensation is avoided.

It however has been found that a cycloalkanone prepared in this way, particularly cyclohexanone, does not meet the demands normally required for its use. Thus when the cyclohexanone is processed into polycaprolactam (nylon-6) by oximation, Beckmann rearrangement and polymerization, the mechanical strength of the polycaprolactam obtained leaves much to be desired. It is now considered that this is due to the fact that a small part of the aldehydes persistently combines with the cyclohexanone fraction. When the cyclohexanone is processed into

polycaprolactam, the aldehydes, even if present in low concentrations, give rise to impurities with a highly deleterious effect on the strength of the polycaprolactam. Other cycloalkanones with 5-12 carbon atoms in the ring show a similar effect.

70

The invention is directed to a process for the purification of cycloalkanone mixtures without any appreciable loss of cycloalkanone by self-condensation, and is based on the discovery that condensation of aldehydes with themselves or with cycloalkanone, can be effected at reaction conditions milder than those at which substantial self-condensation of cycloalkanone occurs.

75

The invention provides a process for the purification of a mixture containing a cycloalkanone containing 5-12 carbon atoms in the ring obtained by the oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen, characterized in that the said mixture containing the cycloalkanone is subjected to an aldol condensation reaction by which at least 80% of the aldehydes present are converted, but not more than 20% of cycloalkyl esters derived from carboxylic acids containing at least 4 carbon atoms per molecule is allowed to saponify.

90

The strong acid or free base which is present in the aldol condensation is necessary as otherwise the aldehydes will not condense with themselves or with the cycloalkanone to form the higher-boiling products. It is in this respect that the process according to the invention differs from the process according to Netherlands Patent Application 6600638. Preferably the aldol condensation is performed with a basic catalyst usually in the form of an aqueous solution. Usually a minimum concentration of free base in the aqueous solution of 0.1 mole/l is used, but the actual minimum requirement depends on the reaction temperature, the particular basic catalyst, the aldehyde concentration, and the amount of aqueous solution used. The reaction conditions such as temperature, nature of the basic catalyst, amount of free base, amount of aqueous solution, duration of treatment and the like, are selected so that not more than a minor proportion of the cycloalkyl esters that are difficult to saponify are saponified. This requirement ensures the avoidance of any appreciable loss of cycloalkanone by self-condensation. A person skilled in the art can determine suitable combinations of reaction conditions from some very simple experiments.

100

105

110

115

In the aldol condensation it is preferred to convert not more than 0.2% cycloalkanone in excess of that required for the removal of the aldehydes. It is possible in practice to restrict the loss of cycloalkanone by self-condensation to less than 0.02%.

120

The reaction temperature preferably is in the range between 30 and 100°C, particularly between 60 and 95°C. The pressure may be, for instance in the range between 10 and 1000 kPa, preferably between 50 and 200 kPa.

125

Particularly suitable solutions of those which may be used in the aldol condensation are aqueous solutions of alkali-metal hydroxides and carbonates, preferably sodium hydroxide or sodium carbonate. Par-

0.5 to 15, more in particular 1 to 5, wt. % aqueous sodium hydroxide solution. The amount of aqueous base solution added is preferably 1 to 20 wt. % with respect to the organic phase. A strongly basic ion exchanger can also be used advantageously as the basic catalyst.

The duration of treatment may, for instance be in the range between 5 and 60 minutes, preferably between 30 and 60 minutes, at an alkali concentration of about 4% by weight, or between 5 and 15 minutes at an alkali concentration of about 15% by weight.

Analogous considerations apply when use is made of aldol condensation catalysed by a strong acid. Suitable strong acids are for example those containing from 0.1 to 20% by weight aqueous sulphuric acid or a corresponding concentration of p-toluene sulphonic acid, or preferably strongly acid ion exchangers containing sulphonic acid groups. At too high acid concentrations there is the risk of undesirable secondary reactions. The amount of strong acid may be a catalytic amount and range, for instance between 0.01 and 10% by weight based on the organic phase, preferably between 0.05 and 0.5% by weight. An advantage of the acid-catalysed reaction is that a lower reaction temperature of, e.g., 30-60°C and/or a shorter reaction period suffice. Use may also be made of temperatures up to 100°C.

The mixtures to be treated usually contain 50 to 1000 parts by weight per million of aldehydes.

The aldol condensation reaction can be effected in a stirred reactor, but use is preferably made of a plug-flow reactor.

By preference such reaction conditions are used that not more than 10% of better still not more than 5% of the cycloalkyl esters derived from carboxylic esters with at least 4 carbon atoms per molecule, is saponified.

The aldol condensation reaction is preferably effected after part or, preferably substantially all of the unconverted cycloalkane has been removed from the reaction mixture of the oxidation reaction. In order to remove organic acids, the mixture may have been subjected to a treatment with water or to a neutralization treatment as described above. If so desired part of the aldehydes, together with other by-products with a lower boiling point than the cycloalkanone, may be distilled off before the aldol condensation.

The product mixture of the aldol condensation may be freed of the acidic or basic catalyst, e.g., by washing with water or by neutralization. If an ion exchanger is used as the catalyst, washing or neutralization may be omitted. The cycloalkanone is preferably then separated e.g. by distillation, from the resulting aldol-condensation products, especially if the cycloalkanone is to be processed into a polyacetal. However this is not necessary for some end-uses for cycloalkanones. Cycloalkanol that is also recovered can be dehydrogenated into a further amount of cycloalkanone in known manner. The distillation residue contains cycloalkyl esters, which can be hydrolyzed in known manner to obtain another amount of cycloalkanol.

Aldol condensation of aldehydes with cycloal-

kanones is known, e.g. from German Auslegeschrift 1,085,520 and J. Am. Chem. Soc. 29 (1964), 1347.

These publications however deal with the reaction of the two reagents in a pure form and in molar ratios of between 1:1 and 1:10. It cannot be inferred from such disclosures that very small proportions of aldehydes could be removed from the much greater amounts of cycloalkane-oxidation products containing cycloalkanone in the way according to the invention.

A further explanation is given in the schematic reaction diagram of the accompanying drawing. The diagram relates to cycloalkanone cyclohexanone, but the process of the invention is also suitable for the purification of other cycloalkanones with 5-12 carbon atoms in the ring, e.g. cyclopentanone or cyclododecanone.

Cyclohexane is passed through line 1 to reactor 2. Air or another gas containing molecular oxygen is fed through line 3 to reactor 2 in which a liquid phase of cyclohexane and oxidation products is maintained. Vent gas escapes through line 4. Cyclohexane vapour contained therein is condensed in a device (not shown) and is returned to reactor 2. The liquid reaction mixture flows through line 5 to neutralization device 6, e.g. a mixer-settler, in which it is washed with an aqueous sodium-carbonate solution supplied through line 7. The amount of sodium carbonate is such that no unconverted base remains in neutralizing device 6. The aqueous phase is discharged through line 8 and a vapour phase through line 9. Cyclohexane is condensed from the vapour phase and returned to reactor 2. The organic liquid phase flows through line 10 to distillation column 11, where the unconverted cyclohexane is removed. The vapour is discharged through line 12, condensed and returned to reactor 2. The distillation residue, which substantially consists of cyclohexanone and cyclohexanol and also contains esters and aldehydes, passes through line 13 to aldol-condensation vessel 14, to which an aqueous sodium hydroxide solution is fed through line 15. The reaction mixture of the aldol condensation flows through line 16 to washing column 17 where it is washed in counter-current relation to water supplied through line 19 to remove traces of hydroxide. If so desired, cyclohexane may be fed to washing device 17 through lines 18 and 16 to improve phase separation. The washing device may be a mixer-settler instead of a column. The washing water, together with the aqueous phase of the reaction product of the aldol condensation, leaves washing device 17 through line 20, while the washed organic mixture is fed through line 21 to distillation column 22, where a fraction (i.e. pentanol and heptanone) with a lower boiling point than cyclohexanone, is distilled off. The light fraction is discharged through line 23, while the heavy fraction is passed through line 24 to a second distillation column 25 wherein cyclohexanone is distilled and recovered through line 26. The heavier fraction flows through line 27 to a third distillation column 28. Cyclohexanol is distilled off and if so desired passed through line 29 to a dehydrogenation unit (not shown) where it can be converted into a further amount of cyclohexanone by dehydrogena-

tion in known manner. The dehydrogenation product may be returned to the distillation column through a line (not shown). A distillation residue containing cyclohexyl esters leaves the system through line 30. If so desired the esters may be hydrolyzed, e.g. with aqueous sodium hydroxide, in a hydrolysis reactor (not shown). The cyclohexanol then obtained can be returned through a line not shown into the system, preferably to the neutralization device 6, aldol-condensation reactor 14 or washing device 17.

Instead of a hydroxide solution, an aqueous solution of a strong acid, e.g. 10% by weight sulphuric acid, can be fed in through line 15, or aldol condensation vessel 14 may be a column filled with a strongly acid ion exchanger, e.g. Dowex 50 L (Dowex is a trade-mark), or another polystyrene resin containing sulphonic-acid groups and cross-linked with divinyl benzene. In this instance washing device 17 can be omitted.

The invention will be further elucidated with reference to the following working examples and comparative experiments.

A glass reactor provided with baffles, a reflux condenser and a stirrer is filled with a mixture that contains 70 grams of cyclohexanone, 130 grams of cyclohexanol, and 2 grams of aldehydes (substantially caproaldehyde) plus the cyclohexyl esters of butyric acid, valeric acid, caproic acid and adipic acid which has been obtained by oxidation of cyclohexane in liquid phase with air followed by neutralization with aqueous sodium carbonate solution, separation of the layers and removal of unconverted cyclohexane by evaporation (flow in line 13 of the drawing). An aqueous sodium-hydroxide solution is added to this mixture in the amounts and concentrations shown in the accompanying Table and vigorously stirred with reflux cooling for 60 minutes at about 95°C and atmospheric pressure. After completion of the reaction, the contents of cyclohexylidene cyclohexanone, aldehyde (calculated as caproaldehyde) and ester in the organic layer are determined by gas-liquid chromatography (GLC). The results are shown in the table:

Amount and concentration of sodium-hydroxide solution		Degree of conversion %		Loss of cyclohexanone % by weight *
		aldehydes	cyclohexyl esters	
Ex. I	20 ml 0.1 N	80	2	< 0.01
Ex. II	20 ml 0.5 N	90	5	0.02
Ex. III	20 ml 1 N	97	10	0.1
Ex. IV	10 ml 1 N	97	10	0.2
Ex. V	20 ml 2.5 N	98	17	0.4
Com. Ex. A	20 ml 7.5 N	> 99	25	1.5
Com. Ex. B	20 ml 10 N	> 99	35	4.2

* calculated to the sum of cyclohexanone and cyclohexanol added

Upon completion of the reaction, pure cyclohexanone can be recovered from the organic layer by distillation.

CLAIMS

1. A process for the purification of a mixture containing a cycloalkanone containing 5-12 carbon atoms in the ring obtained by the oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen, characterized in that the said mixture containing the cycloalkanone is subjected to an aldol condensation reaction by which at least 80% of the aldehydes present are converted, but not more than 20% of cycloalkyl esters derived from carboxylic acids containing at least 4 carbon atoms per molecule is allowed to saponify.

2. A process according to Claim 1, wherein not more than 5% of the said cycloalkyl esters is allowed to saponify.

3. A process according to Claim 1 or Claim 2, wherein not more than 0.2% cycloalkanone in excess of that required for the removal of the aldehydes is converted in the aldol condensation reaction.

4. A process according to any of Claims 1 to 4,

wherein a reaction temperature of between 30° and 100°C is used.

5. A process according to any of Claims 1 to 5, wherein a basic catalyst is used.

6. A process according to Claim 5, wherein the reaction temperature is from 80° to 95°C.

7. A process according to Claim 5 or Claim 6, wherein the said basic catalyst is an aqueous solution of sodium hydroxide or sodium carbonate.

8. A process according to any of Claims 5 to 7, wherein the base concentration is not more than 15% by weight.

9. A process according to any of Claims 1 to 4, wherein an acid catalyst is used.

10. A process according to Claim 9, wherein a reaction temperature of from 30° to 60°C is used.

11. A process according to Claim 9 or Claim 10, wherein the said acid catalyst is an aqueous solution of sulphuric acid.

12. A process according to Claim 9 or Claim 10, wherein the said acid catalyst is a strongly acid ion exchanger.

13. A process according to any of Claims 9 to 12, wherein the concentration of the strong acid corresponds to not more than 20% by weight.

acid.

14. A process according to any of Claims 1 to 13, wherein after the aldol condensation reaction, the cycloalkanone is separated from the resulting condensation products by distillation.

15. A process according to any of Claims 1 to 14, wherein the cycloalkanone is cyclohexanone.

16. A process according to Claim 1, substantially as hereinbefore described and illustrated in the accompanying drawing.

17. A process according to Claim 1, substantially as hereinbefore described in the Examples.

18. Cycloalkanone obtained by a process according to any of Claims 1 to 17.

Printed for Her Majesty's Stationary Office by The Tweeddale Press Ltd.,
Berwick-upon-Tweed, 1980.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.